



(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
06.05.1998 Bulletin 1998/19

(51) Int Cl.⁶: C10G 21/28

(21) Application number: 97500182.7

(22) Date of filing: 30.10.1997

(84) Designated Contracting States:
AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC
NL PT SE
Designated Extension States:
AL LT LV RO SI

(72) Inventors:
• Moreno, Rodriguez, Juan Miguel
28047 Madrid (ES)
• Monjas, Serrano, Carlos
28035 Madrid (ES)

(30) Priority: 31.10.1996 ES 9602311
28.10.1997 ES 9702226

(74) Representative: Hernandez Covarrubias, Arturo
c/o Clarke, Modet & Co.,
Avda. de los Encuarteres 21
28760 Tres Cantos (Madrid) (ES)

(71) Applicant: REPSOL PETROLEO S.A.
E-28046 Madrid (ES)

(54) Process for obtaining aromatic oils having a polycyclic aromatics content of less than 3% which are useful as process oils

(57) Process for obtaining aromatic oils having a polycyclic aromatic compounds content of less than 3 %, useful as rubber extenders, from the mixed extract flow obtained in the manufacture of lubricant bases, which comprises cooling the flow of mixed extracts to render non-polyaromatic components insoluble, settling to bring about separation of the bases, total or partial redissolution in solvent of the light phase obtained in

said settling, cooling to effect separation of the non-pol-
yaromatic components, and settling to recover the light
phase having a low polyaromatic compound content. A
hydrocarbonated stream, having an initial boiling point
greater than 200°C, to regulate the solvent/solute rate
and increase the production capacity of aromatic oils
with a PCA content of less than 3%, may be added to
the starting mixed extract flow.

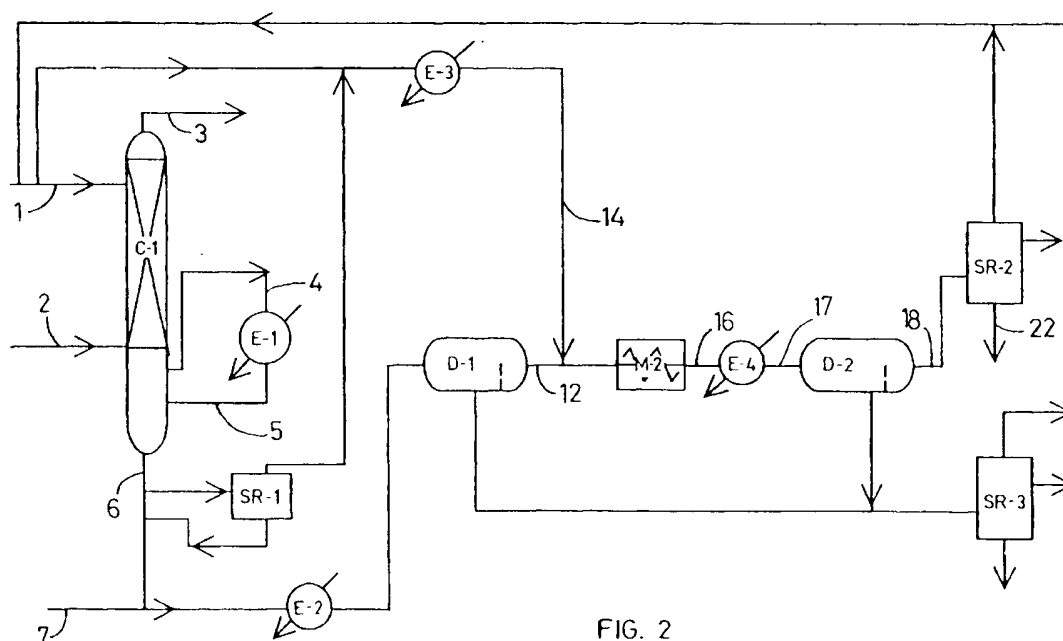


FIG. 2

Description

Scope of the invention

5 This invention relates to a new process for obtaining aromatic oils having a polycyclic aromatic (PCA) compounds content of less than 3% (IP-346), the aromatic oils so obtained and their application as process oils, such as rubber extenders and oils for printing inks.

Background to the invention

10 The components used in the manufacture of rubber, especially in the application for pneumatic tyres, include aromatic oils.

At the present time these aromatic oils are obtained as a by-product of the process of solvent extraction (basically using phenol, furfural, and N-methyl pyrrolidone) of vacuum distillates used as a raw material for the manufacture of lubricant base oils. These aromatic oils, also known as DAE (distillate aromatic extracts) have as a main disadvantage their carcinogenicity due to the polyaromatic hydrocarbons (PAH) and polyaromatic compounds (PAC) which they contain. The latter are found in concentrations very much in excess of 3% (IP-346), the value above which these compounds are regarded as being potentially carcinogenic.

15 In order that a process oil should behave efficiently it is essential that it should have suitable miscibility and solvent properties. In the case of rubbers having a significant percentage of aromatic groups, such as styrene-butadiene (SBR), aromatic oils (DAE) having an aromatic hydrocarbons content in excess of 70% (generally in the range 70-85%) are used, but with a PAC content of around 15% by weight (IP-346).

Another important aspect of the aromatic oils used in the manufacture of rubber is their volatility, which if high leads to the emission of smoke during the manufacturing process.

20 On the other hand, the use of aromatic oils in the formulations of printing inks is limited to products that can not be labeled as potentially carcinogenic.

There is therefore a need to develop low volatility aromatic oils having a lower PAH content and a PAC content (IP-346) below 3% which can replace present oils, eliminating the problem of their potential carcinogenicity.

State of the art

30 As already mentioned, the aromatic oils currently in use are obtained as a by-product in the manufacture of lubricant base oils during solvent extraction of the various vacuum distillates and the deasphalted vacuum bottoms obtained from reduced crude.

The following are obtained as a result of the extraction process: a flow rich in saturated hydrocarbons having a small solvent content known as mixed raffinate, which is the raw material for the manufacture of lubricant base oils, and a flow known as the mixed extract which mainly consists of solvent and oil rich in aromatic hydrocarbons.

The mixed extract flow is passed to a system for the recovery of solvent which is recycled to the extraction column, and an aromatic oil is obtained having a composition which depends on the nature of the vacuum distillate, the conditions under which extraction took place and the efficiency of the extraction column.

40 In general, for these extracts to be used as a process oil a high content of aromatic hydrocarbons is required, and this is generally above 75% by weight (ASTM D-2007). These aromatic extracts (DAE) obtained from vacuum distillates have a polyaromatic compounds (PAC) content in excess of 3%, with the result that they are regarded as being potentially carcinogenic. The aromatic extracts obtained from deasphalted vacuum bottoms have a PAC content which may be in excess of 3%, but despite this they cannot be regarded as potentially carcinogenic.

45 In European patent application no. 90309772.3 a process for obtaining oils with a PAC content of less than 3% is described. The process consists of countercurrent reextraction of the primary extract obtained in the manufacture of lubricant base oils. The extract used as a feed to the reextraction column preferably contains not more than 20% by volume of solvent. This process therefore assumes that most of the solvent will be removed, so that it is then added at the reextraction stage. The quantity of additional solvent required varies between 1 and 1.8 times the quantity of extract being treated. On the other hand, in this application there is no reference to other characteristics such as PAH content, mutagenicity index or volatility of the new process oils.

Summary of the invention

55 A process has now been found which can be used to obtain aromatic oils having a PAC content of less than 3% starting from the mixed extract flow obtained in the process for the manufacture of lubricant base oils described above.

The process according to this invention can bring about a considerable reduction in polyaromatic hydrocarbons

(PAH) content in accordance with US standard EPA-8270 in comparison with the extracts in the state of the art.

The products obtained according to the invention are of a predominantly aromatic nature, with an aromatic hydrocarbons + polar compounds content of more than 45% according to ASTM D-2007, and preferably within the range 60 - 90%.

5 As a result of the process according to the invention the aromatic oils obtained cease to be regarded as potentially carcinogenic and can be used among other applications as extender oils for rubber or in formulations for printing inks.

Basis of the invention

10 This invention is based on the following grounds:

1. The solvents used in the manufacture of lubricant base oils which constitute the majority component of the flow known as the mixed extract are solvents having great selectivity for polyaromatic compounds.

15 2. The selectivity and capacity of a solvent vary with:

a) The solvent/solute ratio

20 b) Temperature: in general, as the temperature decreases selectivity increases and dissolving power decreases.

c) The addition of anti-solvents which regulate dissolving power and can increase selectivity. A typically used anti-solvent is water.

25 d) Use of counter-solvents: these are compounds which act together with the solvent modifying the phase equilibrium. Typical counter-solvents used are e.g. light paraffins.

Advantages of the invention with respect to the state of the art

30 The advantages of the new process according to this invention in comparison with the said European patent application no. 90309772.3 are as follows:

1. Direct use of the mixed extract flow with a consequent **reduction in the quantity of additional solvent**:

35 a) In the case of extract from deasphalted vacuum bottoms no additional solvent is required,

b) In the case of SN-500 or heavier extracts, the quantity of additional solvent will always be less than 1:1 (with reference to the aromatic oil contained in the mixed extract),

40 c) If the extracts are originated from bases of lower viscosity, the quantity of additional solvent will always be less than 1.5:1 (with reference to the aromatic oil contained in the mixed extract) and generally less than 1:1.

2. Use of anti-solvents and counter-solvents to improve selectivity for polyaromatic components. In this case the quantity of additional solvent will be greater than when no anti-solvents or modifiers are used.

45 3. Possibility of adding a hydrocarbonated stream with an initial boiling point at atmospheric pressure, greater than 200°C, preferably greater than 300°C, which allows increasing the production capacity of aromatic oils low in PCA content.

50 4. Reextraction of the extracts to obtain process oils should be performed with the purpose of removing polyaromatic compounds while maintaining the maximum concentration of mono and diaromatic compounds. Very low temperature conditions and solvent/extract ratios may be required in order to achieve this selectivity, and this might give rise to hydrodynamic problems in a countercurrent operation with very aromatic high viscosity extracts. The various modes of operation described in this invention overcome this problem:

55 a) Non-use of countercurrent extraction for heavier extracts, or

b) Use of counter-solvents which reduce viscosity and ensure that the countercurrent operation is performed

correctly.

5. Another advantage of the process according to this invention is excellent characteristics as regards PAH content, mutagenicity index and volatility no reference to which is made in the above mentioned European patent application.

Objects of the invention

Firstly the invention provides a process for obtaining aromatic oils from which potential carcinogenicity has been removed, from the mixed extract flow obtained in the manufacture of lubricant base oils, a flow which contains a polar solvent, preferably of the group comprising phenol, furfural and N-methyl-2-pyrrolidone, preferably furfural, characterized in that it comprises the stages of:

- a) cooling the flow of mixed extract to render non-polyaromatic components insoluble,
- b) settling to bring about separation of the phases,
- c) total or partial redissolution in solvent of the light phase obtained from the settling in stage b),
- d) cooling to effect separation of the non-polyaromatic components, and
- e) settling to recover the light phase having a low PAC content.

Secondly the invention provides aromatic oils which can be regarded as being without carcinogenic potential, obtained in accordance with the process of the first feature of the invention from aromatic extracts obtained from vacuum distillates or deasphalted bottoms having the following characteristics:

- a) Viscosity at 100°C within the range 2 - 70 cSt,
- b) Viscosity indexes generally below 75 in oils having a viscosity of more than 12 cSt (100°C),
- c) PAC content less than 3% by weight (IP-346),
- d) Lower polyaromatic hydrocarbons (PAH) content (US EPA-8270) than the aromatic extracts in the state of the art,
- e) Mutagenicity index according to the modified Ames test (ASTM E-1687-95) very much less than 1,
- f) Lower viscosity than, but volatility similar to the aromatic oils in the state of the art,
- g) Aromatic hydrocarbons + polar compounds content more than 45% (ASTM D-2007) and preferably in the range 60 - 90%.

Thirdly the invention includes the use of the said low PAC content aromatic oils which can be regarded as being without carcinogenic potential, obtained according to the invention, as process oils such as extenders for rubber, and oils for printing inks.

Fourthly, the invention provides rubbers having a high percentage of aromatic groups, such as styrene-butadiene rubbers, which have been extended with the aromatic oils obtained according to the invention.

Embodiments of the process according to the invention

In the process according to the invention an anti-solvent, for example water, can optionally be added to the flow of starting mixed extract in order to increase selectivity for PCAs, in quantities between 0.5 and 10%, preferably between 0.5 and 5% and in particular between 1 and 2.5%.

An important aspect of the process according to the invention is that the quantity of additional solvent in relation to the flow of the hydrocarbon phase in the mixed extract flow is always less than 1.5:1 and preferably less than 1:1.

In addition to this, and optionally, part of the solvent contained in the flow of starting mixed extract can be removed before the cooling stage in order to achieve an approximately 50% distribution of solvent in the stages prior to settling, or add a hydrocarbonated phase with an initial boiling point (IBP) greater than 200°C, preferably greater than 300°C,

to regulate the solvent/solute rate and increase the production capacity of aromatic oils with a PCA content below 3%.

Likewise, and optionally, a counter-solvent can be added before the first cooling stage in order to increase the selectivity of the solvent contained in the mixed extract flow. Preferably the said counter-solvent may be a hydrocarbon flow with a maximum boiling point of less than 160°C, preferably less than 140°C.

The cooling temperature prior to the settling stages lies within the range 10 - 90°C, preferably within the range 10 - 60°C and in particular within the range 20 - 50°C.

In the case of aromatic extracts originating from deasphalted vacuum bottoms it may not be necessary to add additional solvent.

Brief description of the appended drawings

The process according to the invention can be better understood with reference to the following detailed description thereof in combination with the appended drawings, in which:

Figure 1 is a flow diagram of the process according to the state of the art for obtaining aromatic oils as by-products in the production of lubricant base oils during the solvent extraction of various vacuum distillates and the deasphalted vacuum bottom obtained from reduced crude.

Figure 2 is a flow diagram of the process according to this invention for obtaining aromatic oils with a PAC content of less than 3% from the flow of mixed extract according to the state of the art, in which the process is based on the alternatives of reducing the temperature of the mixed extract flow and the optional addition of an anti-solvent, or of a hydrocarbonated stream with IBP greater than 200°C.

Figure 3 is a flow diagram of the process according to the invention for obtaining the said aromatic oils, in which the process is based on the alternatives of reducing the temperature of the mixed extract flow and adding a counter-solvent.

Detailed description of the invention

For comparative purposes Figure 1 shows a flow diagram of the process according to the state of the art used for the production of aromatic extracts.

With reference to the said Figure 1, vacuum distillate (2) and extraction solvent (1) are placed in countercurrent contact in column C-1. The most frequently used solvents are: phenol, furfural and N-methyl-2-pyrrolidone. Solvent (1), which is of greater density, is added to the column at a point close to the top, and distillate (2), of lower density, is introduced at a point close to the bottom. The extraction column may be of various types although one of the most widely used is a mechanically stirred column. In the zone between the two inlet points, countercurrent contact takes place between the solvent and the vacuum distillate. As the solvent flows down the column it will become richer in the aromatic components for which it is most selective. At the same time the rising hydrocarbon flow becomes enriched in saturated hydrocarbons. In general the column operates with a certain temperature gradient which makes it possible to achieve a greater efficiency in the flow which is rich in saturated hydrocarbons. For this purpose part of the descending flow (4) is removed from the column, generally at a point below that at which vacuum distillate enters, and is cooled in an external exchanger (E-1) returning to the column (C-1) via (5).

The extraction process yields a flow rich in saturated hydrocarbons with a small solvent content (3), known as mixed raffinate, which passes to the recovery system (SR-O) and constitutes the starting material for the manufacture of lubricant base oils, and a flow known as the mixed extract (6), which is predominantly made up of solvent and oil rich in aromatic hydrocarbons.

The flow of mixed extract (6) is passed to a solvent recovery system (SR-3) which recycles to the extraction column (C-1) and an aromatic oil (28) is obtained whose composition depends on the nature of the vacuum distillate, the conditions under which extraction took place and the efficiency of the extraction column.

The aromatic extracts obtained in accordance with this process according to the state of the art have a polyaromatic compounds (PAC) content of more than 3%, as a result of which they are regarded as being potentially carcinogenic.

With reference now to Figure 2, this shows the flow diagram of the process according to the invention based on cooling of the starting mixed extract flow and the optional addition of an anti-solvent, or of a hydrocarbonated stream with IBP greater than 200°C.

Specifically, Figure 2 shows a flow diagram of the process according to the invention for obtaining aromatic oils having a PAC content of less than 3% from the mixed extract flow according to the state of the art (6) by cooling in E-2 (and optionally by the addition of water, or of a hydrocarbonated stream with IBP greater than 200°C (7)), and settling in D-1. The light phase (12) obtained in D-1 is mixed with additional solvent at a higher temperature (14) to achieve satisfactory contact between the phases in mixer M-2 and partial or total redissolution. The new flow, 16, is again cooled in exchanger E-4 and is fed to settler D-2 where a new light phase (18) separates out and is sent to a solvent recovery system (SR-2). Flow (22), which is solvent-free, has a PAC content of less than 3% by weight.

If the flow of mixed extract is originated from the solvent extraction of a deasphalted vacuum bottom, then the light phase obtained in settler D-1 can be passed directly to solvent recovery (SR-2), as this flow has a PAC content of less than 3%.

Optionally the flow of mixed extract (6) can be passed to a solvent recovery system (SR-1) to remove some of the solvent before the stage of cooling and settling in D-1. The solvent removed in SR-1 is passed together with the additional solvent required for mixing with the light flow from D-1 for further reextraction and settling in D-2.

Operating conditions of the process according to the flow diagram in Figure 2

Flow (6) leaves column C-1 at a temperature which generally varies within the range 50 - 115°C. This flow has a solvent content which likewise varies within the range 70 - 95%, most frequently being 80-85%. The oil contained in this flow has a polyaromatic hydrocarbons content which varies within the range 4 - 30%. This flow is cooled to a temperature within the range 10 - 90°C, preferably 20 - 50°C, in exchanger E-2. The cold flow from E2 is passed to settler D-1, where a light phase (12) having a low solvent content and a PAC content in the range 0.5 - 10%, fundamentally depending on the type of vacuum distillate (2), separates out. The light flow leaving D-1 is mixed (M-2) with solvent at a higher temperature within the range 30 - 160°C to dissolve most of the hydrocarbon components and is again cooled to the desired settling temperature, generally within the range 10 - 90°C and preferably within the range 20 - 50°C, in exchanger E-4. The cold flow (17) is passed to settler D-2 where a light phase (18) having a low solvent and polyaromatic compounds content again separates out. Flow (18) is passed to system SR-2 for the removal of the solvent. Optionally, an anti-solvent (7) or a hydrocarbonated fraction with IBP greater than 200°C (7), may be added to the mixed extract flow, which, in order to simplify, have both been considered as the same stream in fig. 2.

With reference now to Figure 3, this illustrates the process according to the invention based on cooling of the starting mixed extract flow and the addition of a counter-solvent.

Specifically, Figure 3 shows the flow diagram for the process based on temperature reduction, the addition of a counter-solvent and reextraction.

A counter-solvent (7) is added to the flow of mixed extract (6), and the resulting flow is cooled in exchanger E-2. The resulting flow (9) is passed to a mixer M-1 in order to achieve a satisfactory level of contact between the phases and then to a settler, D-1, where the phases separate out. The light phase (12) is mixed with additional solvent (14) in a mixer M-2, and is again cooled in exchanger E-4, from which it passes to settler D-2. The light phase (18) leaving D-2 is passed to a system SR-2 for the recovery of solvent and counter-solvent which are recycled to the process and a flow (22) having a PAC content of less than 3% is obtained.

If the flow of mixed extract originates from the solvent extraction of a deasphalted vacuum bottoms then the light phase obtained in settler D-1 can be passed directly to solvent recovery SR-3 if its PAC content is less than 3%.

Optionally the flow of mixed extract (6) can be passed to a solvent recovery system (SR-1) to remove part of the solvent before the stage of cooling and settling in D-1. The solvent removed in SR-1 is passed together with the additional solvent required for mixing with the light flow from D-1 for further reextraction and settling in D-2. Optionally the system comprising M-2, E-4 and D-2 may be replaced by countercurrent extraction.

Operating conditions for the process according to the flow diagram in Figure 3

Flow 6 leaves column C-1 at a temperature which generally varies within the range 50 - 115°C. This flow has a solvent content which likewise varies within the range 70 - 95%, most frequently being 80 - 85%. The oil contained in this flow has a polyaromatic hydrocarbons content which varies within the range 4 - 30%.

A counter-solvent such as a light paraffin, e.g. n-heptane (7), is added to this flow and the mixture is cooled to a temperature within the range 10 - 90°C, preferably 20 - 50°C, in exchanger E-2. Optionally flow (7) may be added after the cooling stage in E-2. The cold flow from E-2 passes to mixer M-1 in order to achieve satisfactory contact between the phases and is passed to settler D-1 where a light phase consisting of solvent, counter-solvent and a mixture of hydrocarbons having a PAC content in the range 0.5 - 15%, depending fundamentally on the nature of vacuum distillate 2, separates out. The light flow leaving D-1 is mixed (M-2) with solvent previously cooled in E-3 to a temperature below the boiling point of the most volatile component, preferably 30 - 50°C. Optionally it can be cooled again in exchanger E-4 to the desired settling temperature, generally within the range 15 - 90°C and preferably within the range 15 - 50°C. Flow (17), which is cold, is passed to settler D-2 where a light phase (18) consisting of counter-solvent, solvent and a mixture of hydrocarbons having a low polyaromatic compounds content again settles out and is passed to system SR-2 to remove solvent and counter-solvent.

Examples of practical embodiments of the invention

The process according to the invention will now be described with reference to the following examples which are

offered purely by way of illustration.

Example 1

5 This example includes the results obtained in the treatment of the mixed extract flow (6) obtained from furfural extraction to obtain SN-600. The outlet temperature of this flow was 85 - 95°C. The flow was cooled at different temperatures in E2 and settled in D-1. The light flow from D-1 was mixed with additional furfural at a higher temperature in M-2. The resulting flow (16) was cooled to the same temperature as in E-2 and settled in D-2. The results obtained were:

10

15

20

25

30

35

40

45

50

55

Experiment no.	1	2
Furfural content of the mixed extract flow, % w/w	85.0	85.0
Refractive index of the hydrocarbon phase at 60°C	1.5574	1.5574
PAC content of the hydrocarbon phase, % w/w, IP-346	16	16
Separation temperature in D-1, °C	40	50
Yield of raffinate (*) in D-1, % w/w	43.7	36.2
Analysis of the solvent-free light phase in D-1		
Furfural content, % w/w	12.01	12.93
Refractive index at 60°C	1.5165	1.5137
PAC content, % w/w, IP-346	4.1	3.9
Reextraction of the light phase from D-1		
Temperature, °C	40	50
Furfural/mixed raffinate (w/w)	0.73/1	0.74/1
Raffinate yield (*) in D-2, % w/w	93.2	92.5
Analysis of the raffinate from D-2		
Furfural content, % w/w	10.7	11.5
Refractive index at 60°C	1.5124	1.5094
Density at 70/4°C	0.9154	0.9090

	Aniline point, °C	72.6	76.4
5	Viscosity at 100°C, cSt	18.75	17.10
	Viscosity index	48	34
10	Pour point, °C, ASTM D-97	+27	+36
	PAC content, % w/w, IP-346	2.4	2.4
15	Sulphur, % w/w, ASTM D-4294	3.2	3.0
	Hydrocarbon composition, ASTM D-2007		
20	Saturated hydrocarbons, % w/w	23.5	26.7
	Polar compounds, % w/w	5.3	5.0
25	Aromatic hydrocarbons, % w/w	71.2	68.3
30	Overall yield of low PAC content raffinate, % w/w	40.7	33.5

(*): Solvent free base oil

These results indicate the advantage of cooling to the minimum temperature possible in E-2 and E-3. A product having a similar PAC content is obtained at 40 and 50°C, but the yield at 40°C is seven points higher than that obtained by cooling and reextracting at 50°C. Likewise, the product obtained at 40°C is more aromatic than that obtained at 50°C.

Example 2

This example includes the results obtained from the treatment of the mixed extract flow 6 obtained from the furfural extraction of deasphalted vacuum bottoms. The outlet temperature of this flow was 100 - 110°C. The flow was cooled to different temperatures in E2 and settled in D-1. The light flow from D-1 had a PAC content of less than 3% once the solvent had been removed, and it was not reextracted for this reason.

Experiment no.	3	4
Furfural content of the mixed extract flow, % w/w	92.1	92.2
Refractive index of the hydrocarbon phase at 60°C	1.5483	1.5484
PAC content of the hydrocarbon phase, % w/w, IP-346	5.4	5.5
Separation temperature in D-1, °C	40	50
Yield of raffinate (*) in D-1, % w/w	54.7	47.1
Analysis of the raffinate in D-1		
Furfural content, % w/w	11.9	12.8
Refractive index at 60°C	1.5260	1.5235
Density at 70/4°C	0.9339	0.9306
Aniline point, °C	74.8	78.0
Viscosity at 100°C, cSt	59.21	58.35
Viscosity at 40°C, cSt	2450	2208
Viscosity index	48	55
Pour point, °C, ASTM D-97	+15	+18
PAC content, % w/w, IP-346	1.1	0.9
Sulphur, % w/w, ASTM D-4294	3.62	3.49
Hydrocarbon composition, ASTM D-2007		

5	Saturated hydrocarbons, % w/w	14.8	15.9
	Polar compounds, % w/w	9.6	10.2
10	Aromatic hydrocarbons, % w/w	75.6	73.9

These results show the advantage of cooling to the minimum possible temperature in E-2. A product having a similar PAC content is obtained at 40 and 50°C, but the yield at 40°C is seven points greater than that obtained by cooling and reextracting at 50°C. Likewise the product obtained at 40°C is more aromatic than that obtained at 50°C.

Example 3

This example includes the results obtained from the treatment of the mixed extract flow, 6, obtained from furfural extraction to obtain a SN-150 base oil. The outlet temperature of this flow was 80°C. The flow was cooled to 40°C in E2 and settled in D-1. The light flow from D-1 was mixed with additional furfural at a higher temperature in M-2. The resulting flow 16 was cooled to the same temperature as in E-2 and settled in D-2. The results obtained were:

25	Experiment no.	5
	Furfural content of the mixed extract flow, % w/w	81.1
	Refractive index of the original extract at 70°C	1.5389
	PAC content of the hydrocarbon phase, % w/w, IP-346	22
30	Separation temperature in D-1, °C	40
	Yield of raffinate (*) in D-1, % w/w	33.0
	Analysis of the raffinate in D-1	
	Furfural content, % w/w	10.4
35	Refractive index at 70°C	1.4900
	Density at 70°C	0.8806
	PAC content, % w/w, IP-346	5.8
	Reextraction of the light phase from D-1	
40	Ratio of furfural/light phase from D-1 (w/w)	2.4/1
	Separation temperature in D-2, °C	40
	Yield of raffinate (*) in D-2 % w/w	78.4
	Analysis of the raffinate from D-2	
45	Furfural content, % w/w	6.8
	Refractive index at 70°C	1.4782
	Density at 70/4°C	0.8631
50	Aniline point, °C	79.4
	Viscosity at 100°C, cSt	5.23
	Viscosity at 40°C cSt	33.38
55	Viscosity index	80
	PAC content, % w/w	2.5

(continued)

Experiment no.	5
Analysis of the raffinate from D-2	
Pour point, °C, ASTM D-97	+15
Sulphur, % w/w, ASTM D-4294	1.76
Hydrocarbon composition, ASTM D-2007	
Saturated hydrocarbons, % w/w	46.9
Polar compounds, % w/w	1.0
Aromatic hydrocarbons, % w/w	52.1
OVERALL YIELD	25.9

Example 4

This example includes the results obtained in treatment of the mixed extract flow, 6, obtained from furfural extraction to obtain SN-600. In this case the results obtained by cooling and reextracting at 40°C are compared with those obtained under similar conditions but with the addition of water to the flow 6. The results obtained were:

Experiment no.	6	7
Furfural content of the mixed extract flow, % w/w	85.9	85.9
Refractive index at 60°C	1.5640	1.5640
PAC content of the hydrocarbon phase, % w/w, IP-346	16	16
Water added, % w/w (with reference to furfural)	0	1.6
Separation temperature in D-1, °C	40	40
Yield of raffinate (*) in D-1, % w/w	35.0	44.3
Analysis of the raffinate from D-1		
Furfural content, % w/w	10.8	11.7
Refractive index at 60°C	1.5179	1.5243
PAC content, % w/w	3.5	4.7
Reextraction of the light phase from D-1		
Ratio of furfural/light phase D-1, w/w	0.9/1	1.7/1
Separation temperature in D-2	40	40
Raffinate yield (*) in D-2, % w/w	92.5	86.0
Analysis of the raffinate from D-2		
Furfural content, % w/w	10.7	11.0
Refractive index at 60°C	1.5135	1.5170
Viscosity at 100°C, cSt	19.35	20.60
Viscosity at 70°C, cSt	63.30	69.92
Viscosity index	34	26
Density at 70/4°C	0.9138	0.9185
Aniline point, °C	72.8	70.0
PCAs, % w/w	2.7	2.8

(*) From solvent-free base.

(continued)

Experiment no.	6	7
Analysis of the raffinate from D-2		
Overall yield	32.4	38.1

These results show that the addition of water to produces an increase of 5 to 6 points in yield of raffi

extract from column C-1 (1.6% with respect to solvent)
2 with a PAC content of less than 3%.

Example 5

This example includes the results obtained from treatment of the mixed extract flow, 6, obtained from furfural extraction to obtain SN-600. In this case the results obtained by cooling and reextracting at 40°C are compared with those obtained under similar temperature conditions but with the addition of a counter-solvent prior to cooling in E-2. The results obtained were:

Experiment no.	1	8
Furfural content of the mixed extract flow, % w/w	85.1	85.1
Refractive index of the hydrocarbon phase at 60°C	1.5574	1.5574
PAC content of the hydrocarbon phase, % w/w, IP-346	16	16
Added heptane (ratio of heptane/mixed extract, w/w)	---	0.15/1
Separation temperature in D-1, °C	40	40
Yield of raffinate (*) in D-1, % w/w	43.7	61.0
Analysis of the raffinate from D-1		
Furfural + n-heptane content, % w/w	12.0	52.5
Refractive index at 60°C	1.5143	1.5260
PAC content, % w/w, IP-346	4.1	4.8
Reextraction of the light phase from D-1		
Ratio of furfural/light phase D-1, w/w	0.73/1	1.15/1
Separation temperature in D-2, °C	40	40
Raffinate yield (*) in D-2, % w/w	93.2	88.3
Analysis of the raffinate from D-2		
Furfural + n-heptane content, % w/w	10.7	48.5
Refractive index at 60°C	1.5124	1.5182
Viscosity at 100°C, cSt	18.75	20.29
Viscosity at 70°C, cSt	---	67.40
Viscosity index	48	33
Density at 70/4°C	0.9154	0.9210
Aniline point, °C	72.6	66.8
PCAs, % w/w	2.4	2.9
Overall yield	40.7	53.9

(*) From solvent-free base.

These results show that an increase in yield of approximately 13 points of product having a PAC content of less than 3% is obtained by adding a counter-solvent such as n-heptane to the mixed extract leaving C-1.

Example 6

This example includes the results obtained from the treatment of the mixed extract flow, 6, obtained from furfural extraction to obtain SN-600. In this case the results obtained by cooling and reextracting at 40°C are compared with those obtained under similar temperature conditions but with removing part of the furfural from the flow 6 in SR-1 before cooling in E-2 and reextracting the light phase from D-1 with additional furfural in order to make up the total furfural/extract ratio used in example 1.

Experiment no.	1	9
Furfural content of the mixed extract flow, % w/w	85.0	85.0
Furfural content of the flow entering E-2	85.0	75.1
Refractive index of the hydrocarbon phase at 60°C	1.5574	1.5574
PAC content of the hydrocarbon phase, % w/w, IP-346	16	16
Separation temperature in D-1, °C	40	40
Yield of raffinate (*) in D-1, % w/w	43.7	58.3

Analysis of the raffinate from D-1		
5	Furfural content, % w/w	12.01 13.2
	Refractive index at 60°C	1.5165 1.5281
10	PAC content, % w/w, IP-346	4.1 5.8
Reextraction of the light phase from D-1		
15	Separation temperature in D-2, °C	40 40
20	Furfural/mixed raffinate, w/w	0.73/1 5.8/1
25	Raffinate yield (*) in D-2, % w/w	93.2 67.7
Analysis of the raffinate from D-2		
30	Furfural content, % w/w	10.7 10.7
	Refractive index at 60°C	1.5124 1.5099
35	Density at 70/4°C	0.9154 0.9094
	Aniline point, °C	72.6 74.8
40	Viscosity at 100°C, cSt	18.75 18.05
	Viscosity at 70°C, cSt	58.85 56.41
45	Viscosity at 40°C, cSt	328.0 313.18
	Viscosity index	48 46
50	PAC content, % w/w, IP-346	2.4 1.8
HYDROCARBON COMPOSITION, ASTM D-2007		
55	Saturated hydrocarbons, % w/w	23.5 ---

	Polar compounds, % w/w	5.3	---
5	Aromatic hydrocarbons, % w/w	71.2	---
10	Overall yield of low PAC content raffinate, % w/w	40.7	39.5

These results show that distribution of the solvent into equal parts in D-1 and D-2 makes it possible to obtain a raffinate with a reduced PAC content without the need to use additional solvent.

Example 7

This example contains the results obtained in the treatment of the flow of mixed extract 6, resulting from the extraction with furfural to obtain SN-600. In this case, the results obtained by cooling and re-extracting at 40°C are compared with ones obtained in similar conditions of temperature but adding a hydrocarbonated stream with IBP greater than 200°C to the flow of mixed extract 6, before cooling at E-2 and extracting the light phase from D-1 with additional furfural to reduce the PCA content to below 3%.

25	Experiment no.	1	10
30	Furfural content of the mixed extract flow, % w/w	85.0	85.0
35	Added hydrocarbonated stream (w/w mixed extract)	0	0.105/1
40	I. Refraction at 60°C of the hydrocarbon phase	1.5574	1.5271

45

50

55

5	PAC content of the hydrocarbon phase, % w/w, IP-346	16	11.1
10	Separation temperature in D-1, °C	40	40
	Yield of raffinate (*) in D-1, % w/w	43.7	70.8
15	Analysis of the raffinate from D-1		
	Furfural content, % w/w	12.01	8.0
20	I. Refractive index at 60°C	1.5165	1.4987
	PAC content, % w/w, IP-346	4.1	3.1
25	Reextraction of the light phase from D-1		
	Separation temperature in D-2, °C	40	40
30	Furfural/mixed raffinate, w/w	0.73/1	0.5/1
35	Raffinate yield (*) in D-2, % w/w	93.2	96.8
40	Analysis of the raffinate from D-2		
	Furfural content, % w/w	10.7	7.1
	I. Refractive index at 60°C	1.5124	1.4972
45	Density at 70/4°C	0.9154	0.8885
	Aniline point, °C	72.6	91.4
50	Viscosity at 100°C, cSt	18.75	15.11
	Viscosity at 40°C, cSt	328.0	200.2
55			

Viscosity index	48	67
PAC content, % w/w, IP-346	2.4	2.5
HYDROCARBON COMPOSITION, ASTM D-2007		
Saturated hydrocarbons, % w/w	23.5	46.1
Polar compounds, % w/w	5.3	4.0
Aromatic hydrocarbons, % w/w	71.2	49.9
Overall yield of low PAC content raffinate, % w/w	40.7	68.6

These results prove that the addition of a hydrocarbonated stream (IBP greater than 200°C) allows increasing the production of aromatic oil with low PCA content without notable increase of furfural required in the re-extraction of the raffinate obtained in the first settling step.

Analyses of an oil B obtained from a mixed SN-600 extract according to this invention are shown in the table below. In this table the results of the analyses are compared with those for an extract from the state of the art (A).

The results of the analyses of an oil D obtained from a mixed deasphalted vacuum bottoms extract according to this invention are shown. The results are compared with those corresponding to an extract from the state of the art (C).

	SN-600 extract		Deasphalted oil extract	
	A	B	C	D
Oil				
PAC content, % w/w, IP-346	16	2.6	5.5	1.5
Mutagenicity index (MI) (modified Ames test)	>1	0.2	---	0
Viscosity at 100°C, cSt, ASTM D-445	33.6	19.54	71.02	51.22
Flash point, open cup, °C, ASTM D-92	276	278	302	318
Loss on evaporation, 3 hours, 163°C, % w/w	0.04	0.01	0.04	0.01
Hydrocarbon composition, ASTM D-2007				
Saturated hydrocarbons, % w/w	10.7	26.5	13.9	23.2
Polar compounds, % w/w	11.0	5.7	12.1	10.5
Aromatic hydrocarbons, % w/w	78.3	67.8	74	66.3
DISTILLATION, modified ASTM D-2887				
IBP	378	382	464	483
5%	435	442	507	515
50%	500	506	584	584
90%	547	548	661	662
95%	562	561	682	685
FBP	599	596	725	726

In the table below PAH contents according to the US EPA 8270/95 method in products obtained using the process according to this invention are compared with those corresponding to present-day aromatic extracts.

5

10

15

20

25

30

35

40

45

50

55

	AROMATIC SN-600 EXTRACT		DEASPHALTED OIL AROMATIC EXTRACT	
	Present productio n: high PAC content	Obtained according to this invention	Present productio n	Obtained according to this invention
OIL	A	B	C	D
Naphthalene	<1	<1	<1	<1
Acenaphthylene	<1	<1	<1	<1
Acenaphthene	<1	<1	<1	<1
Fluorene	<1	<1	<1	<1
Phenanthrene	2.3	<1	<1	<1
Anthracene	<1	<1	<1	<1
Fluoranthene	<1	<1	<1	<1
Pyrene	1.2	<1	<1	<1
Benzo[a]fluorene	2.1	<1	<1	<1
Benzo[b]fluorene	1.0	<1	<1	<1
B e n z o - [a]anthracene	<1	<1	<1	<1
Chrysene/- triphenylene	8.2	<1	1.3	<1
Benzo[b,j]- fluoranthene	2.9	<1	<1	<1
Benzo- [k]fluoranthene	<1	<1	<1	<1

	Benzo[e]pyrene	12	<1	1.6	<1
5	Benzo[a]pyrene	<1	<1	<1	<1
	Perylene	<1	<1	<1	<1
10	Indeno[1,2,3-cd]pyrene	6.9	<1	<1	<1
15	Benzo[g,h,i]-perylene	16	<1	1.5	<1
	Dibenzo[a,h/a,c]-anthracene	<1	<1	<1	<1
20	Coronene	<1	<1	<1	<1

Industrial application of the invention

One of the objectives of this invention is to develop aromatic oils having a low PAC content which will not be regarded as potentially carcinogenic for application as rubber extenders.

Three samples of rubber using a typical formulation for tyres have been prepared with a view to comparing the properties of rubbers formulated using these oils with a low PAC content and rubbers formulated with aromatic oils having a high PAC content.

FORMULATION	
Component	Parts by weight
SBR 1502 (Krylene 1502)	60
High cis polybutadiene (PB 1202)	40
N-234 carbon black (ISAF-HS)	70
Aromatic oil	40
Zinc oxide	3
Stearic acid	2
Santoflex 13 (N-(1,3-dimethylbutyl-N'-phenyl-p-phenylenediamine)	1
HS antioxidant (Poly(2,2,4-trimethyl-1,2-dihydroquinoline))	2
Redezon (Repsol antiozone wax)	3
Rubenamide C (N-cyclohexylbenzothiacyl-sulphenamide)	1
Sulphur	1.75

Three samples were prepared, each with one type of oil (A, B, D) in a cylinder mixer 30 cm long having a friction ratio of 1:1.14. The same order of addition and the same mixing time were used in the preparation of the samples. The vulcanization temperature was 150°C in all three cases.

The table below includes the properties of the vulcanizates:

Mixtures	Mixture A	Mixture B	Mixture D
Oil used	A	B	D
Property			
Shore hardness A	51.0	51.9	52.7
Resilience, %	30	30	28.5
100% deformation force, MPa	1.13	1.17	1.10
300% deformation force, MPa	4.50	4.67	4.23
500% deformation force, MPa	10.51	10.75	9.41
Tensile strength, MPa	16.31	16.32	17.14
Elongation on fracture, %	694	680	769
Tear resistance, N	55.3	53.7	57.2

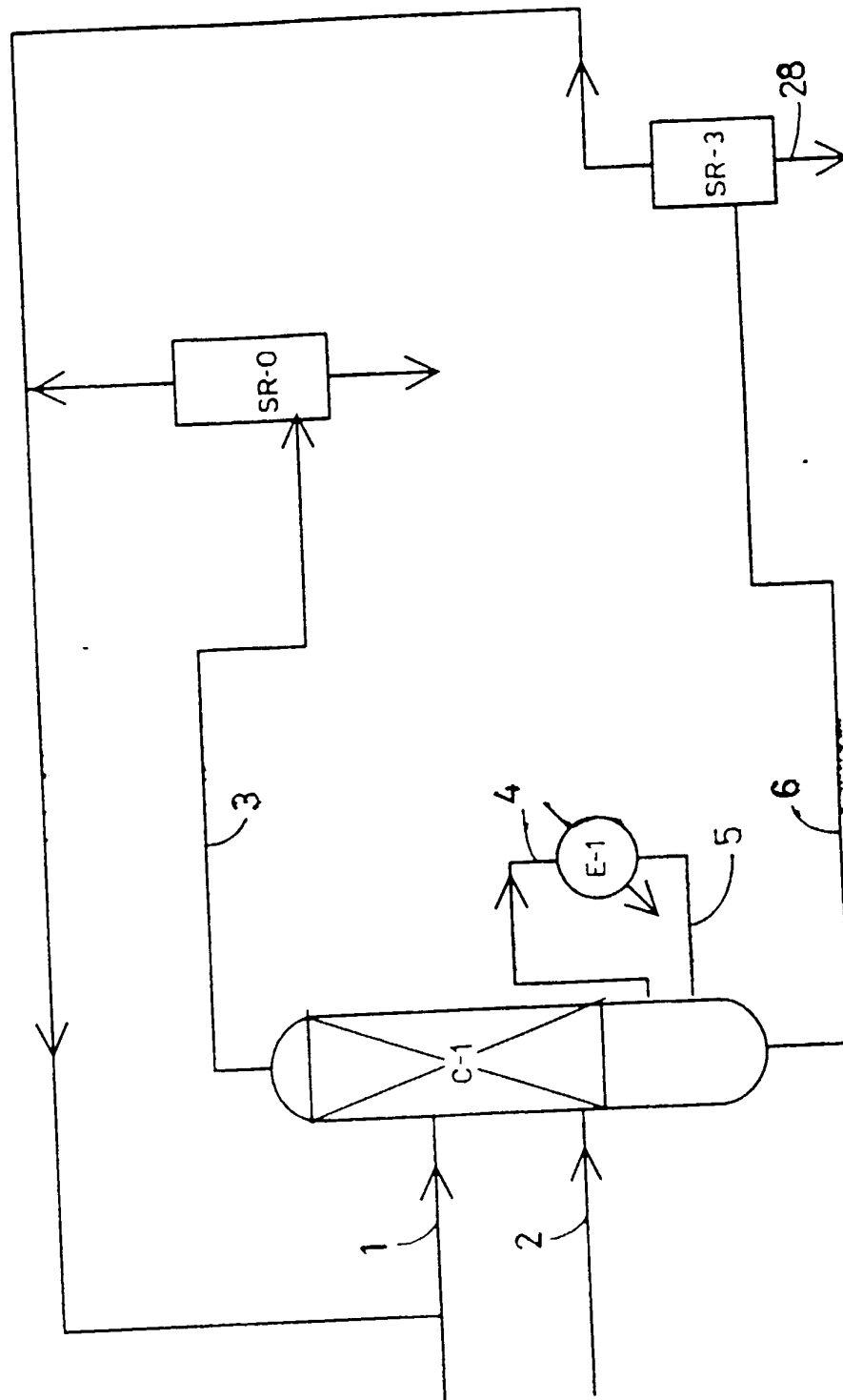
These results show that when state-of-the-art oil (A) is replaced by oils obtained in accordance with this invention (B, D) rubbers with very similar properties are obtained. Nevertheless, it is not the purpose of this patent to provide a formulation, but only to compare the rubbers formulated under identical conditions using state-of-the-art oils and those obtained in accordance with this invention.

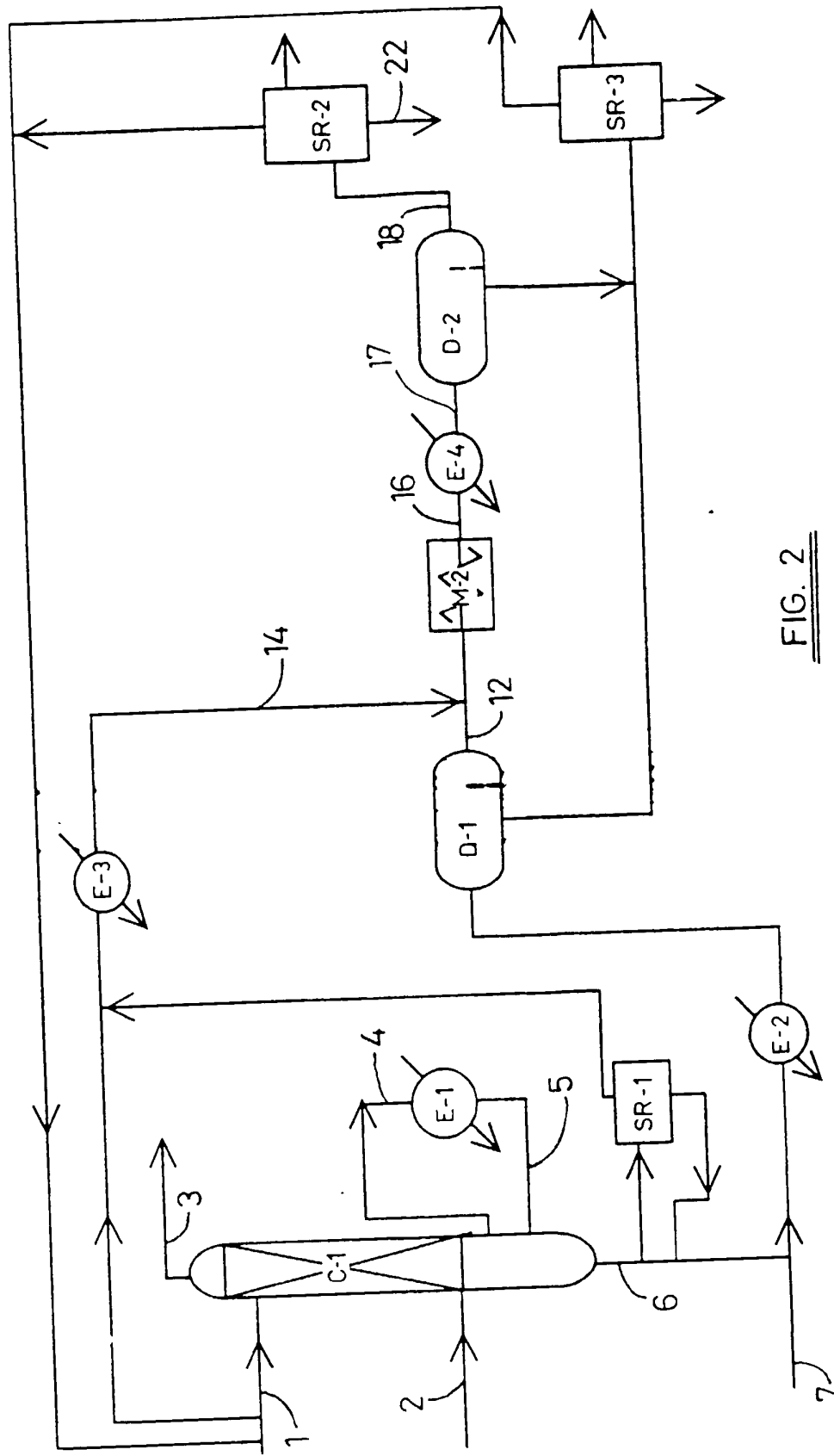
Claims

- Process for obtaining aromatic oils with a polycyclic aromatic compounds content of less than 3% (IP-346) from the mixed extract flow obtained in the manufacture of lubricant base oils, a flow which contains a polar solvent, preferably of the group comprising phenol, furfural and N-methyl-2-pyrrolidone, preferably furfural, characterized in that it comprises the stages of:
 - cooling the flow of mixed extract to render non-polyaromatic components insoluble,
 - settling to bring about separation of the phases,
 - total or partial redissolution in solvent of the light phase obtained from the settling in stage b),
 - cooling to effect separation of the non-polyaromatic components, and
 - settling to recover the light phase having a low polyaromatic compounds content.
- Process according to Claim 1, characterized in that the light phase obtained in stage e) has a polyaromatic compounds content of less than 3% according to IP-346, an aromatic hydrocarbons + polar compounds content of more than 45% according to ASTM D-2007, a polyaromatic hydrocarbons content (US EPA 8270) which is very much less than that of the extracts in the state of the art, a mutagenicity index according to the modified Ames test which is less than 1, a lower viscosity than known extracts for a similar volatility level and viscosity indexes generally less than 75 in products having a 100°C viscosity of more than 12 cSt.
- Process according to Claim 1, characterized in that an anti-solvent such as water is optionally added to the starting mixed extract flow to increase selectivity for polyaromatic compounds.
- Process according to Claim 3, characterized in that the quantity of anti-solvent optionally added varies between 0.5 and 10%, and preferably between 0.5 and 5% and especially between 1 and 2.5%.
- Process according to Claims 1 and 4, characterized in that the quantity of additional solvent in relation to the flow of the hydrocarbon phase in the mixed extract flow is always less than 1.5:1 and preferably less than 1:1.
- Process according to Claim 1, characterized in that some of the solvent contained in the mixed extract flow is

optionally removed before the cooling stage in order to achieve an approximately 50% distribution of solvent in the stages prior to settling.

- 5 7. Process according to Claim 1, characterized in that a hydrocarbonated stream, having an initial boiling point at 760 mm Hg greater than 200°C, preferably greater than 300°C, is optionally added to the starting mixed extract flow to regulate the solvent/solute rate and increase the production capacity.
- 10 8. Process according to claim 7, characterized in that the added hydrocarbonated stream can be a product obtained in any of the vacuum distillation processes of the atmospheric residue, extraction with solvent, dewaxing or deasphalting.
- 15 9. Process according to Claim 1, characterized in that a counter-solvent is optionally added before the first cooling stage to increase the selectivity of the solvent contained in the mixed extract flow.
- 20 10. Process according to Claim 9, characterized in that the counter-solvent may be a hydrocarbon flow with a maximum boiling point of less than 160°C, preferably less than 140°C.
21. Process according to any one of Claims 1, 3, 6, 7 and 9, characterized in that the cooling temperature before the settling stages lies within the range 10 - 90°C, preferably within the range 10 - 60°C and in particular within the range 20 - 50°C.
- 25 12. Process according to any one of Claims 1, 3, 6, 7 and 9, characterized in that in the case of aromatic extracts originating from bottoms the use of additional solvent is optional.
- 26 13. Aromatic oils which can be regarded as being without carcinogenic potential, obtained in accordance with the process in Claims 1 to 10 from aromatic extracts obtained from vacuum distillates or deasphalted bottoms characterized in that they have the following properties:
 - 30 a) Viscosity at 100°C within the range 2 - 70 cSt,
 - b) Viscosity indexes generally below 75 in oils having a viscosity of more than 12 cSt (100°C),
 - c) Polyaromatic compounds content less than 3% by weight (IP-346),
 - 35 d) Lower polyaromatic hydrocarbons (PAH) content (US EPA-8270) than the aromatic extracts in the state of the art,
 - e) Mutagenicity index according to the modified Ames test (ASTM E-1687-95) very much less than 1,
 - 40 f) Lower viscosity than, but volatility similar to the aromatic oils in the state of the art,
 - g) Aromatic hydrocarbons + polar compounds content more than 45% (ASTM D-2007) and preferably in the range 60 - 90%.
- 45 14. Use of aromatic oils having a low polyaromatic compounds content according to Claim 13 as process oils and particularly as rubber extenders.
15. Use according to Claim 14 as rubber extenders having a high percentage of aromatic groups.
- 50 16. Use according to Claims 14 and 15 as styrene-butadiene rubber extenders.
17. Rubbers extended with the aromatic oils obtained according to the process in Claims 1 to 12 or described in Claim 13.

FIG. 1

FIG. 2

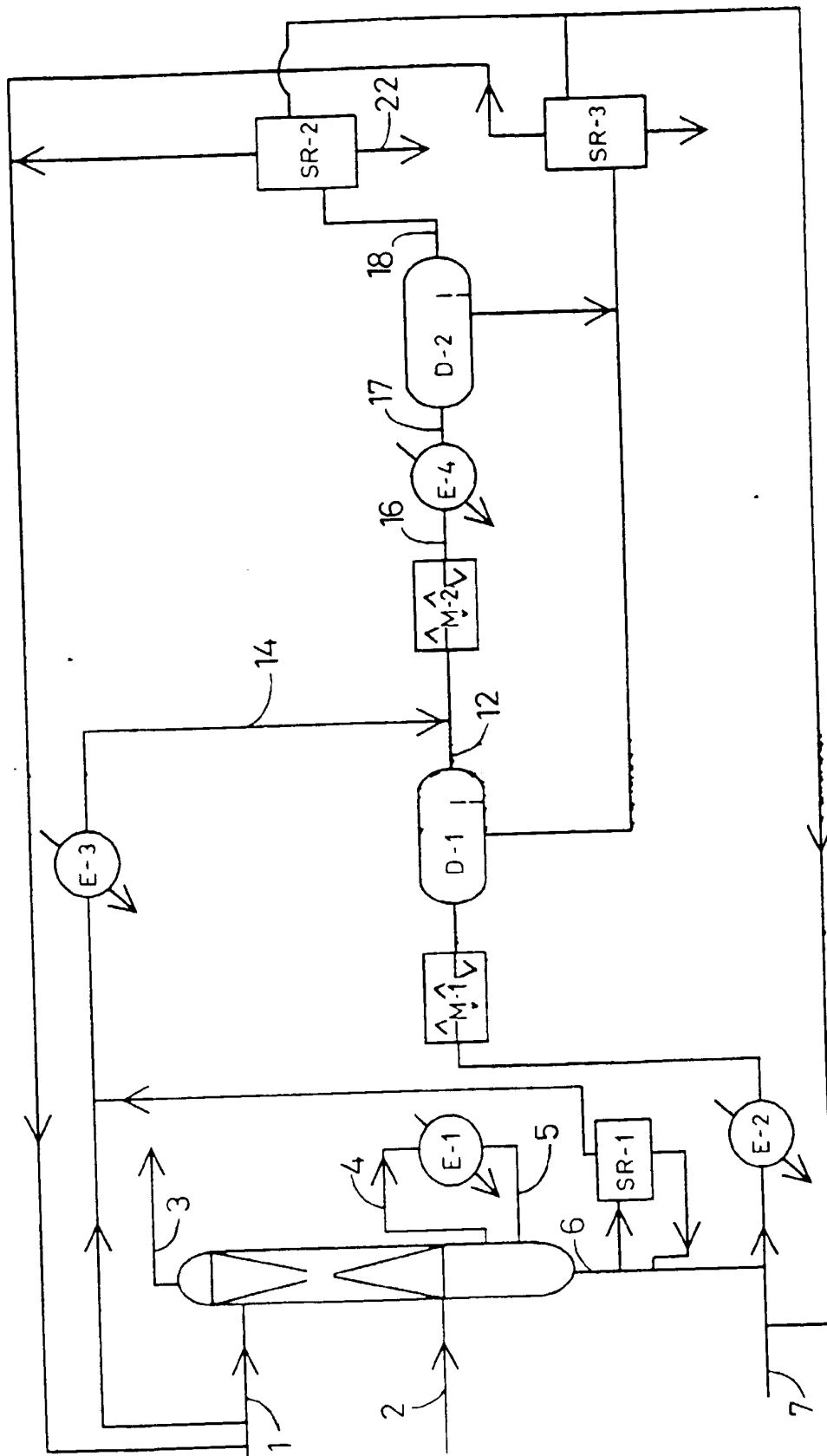


FIG. 3